Effects of F-doping on preparation and superconducting characteristics of Ag-sheathed Tl-1223 tapes

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Abstract : The effects of partial substitution of fluorine on physical properties were studied in Ag-sheathed tapes of $Tl_{0.8}Pb_{0.2}Bi_{0.2}Sr_{1.8}Ba_{0.2}Ca_{2.2}Cu_3O_yF_x$ $(0 \leq x \leq 1)$ nominal compositions. The tapes were prepared using the powder-in-tube method incorporating an in-situ reaction method. CuF_2 was used as a source of F. It was found that F-doping in Tl-1223 system resulted in a decrease in formation temperature of Tl-1223 phase. However, it significantly decreased the volume percentage of Tl-1223 phase, and thus significantly deteriorated their superconducting properties. Such disadvantages seem to originate by the formation of non-beneficial phases such as SrF_2 in the early stage of the powder preparation process.

Key Words : superconducting tapes, Tl-1223, critical current density, fluorine doping

1. Introduction

It has been known that Tl-1223 high T_c superconductor (HTS) has an irreversibility line located at a relatively high position in H-T space, which is due to the relatively short distance between Cu-O layers in the crystal lattice, compared with those of other high T_c superconductors [1]. It has been expected that Tl-1223 wires with large current-carrying capacities at relatively high fields and temperatures will be able to be developed, and thus 40 K technology instead of 20 K in the case of Bi-based HTS wires will be realized.

In contrast to remarkable advances [2,3] in aspects of J_c and preparation cost in Tl-1223 film-type tapes prepared by so-called open methods, the progress in preparation of Tl-1223 tapes with high J_c's by using the powder-in-tube (PIT) method has been slowed down. Up to now, various chemical composi-tions and preparation methods have been attempted in order to prepare Tl-1223 tapes

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with high J_c's using the PIT method [4-17]. However, the tapes have shown relatively low J_c's compared with those of Bi-based HTS tapes, mainly due to poor grain-connectivity and little directional alignment of Tl-1223 grains in the superconducting cores [1,4,5].

It has been found that the grain connecti-vity and degree of directional grain-align-ment, and thus J_c values primarily depended on the nominal compositions used for the tape cores-especially the ratio of Sr to Ba [6,12,14,17]. The tapes of compositions with Sr:Ba = 1.6:0.4 such as $Tl_{0.9}Bi_{0.22}Sr_{1.6}Ba_{0.4}Ca_2Cu_3O_{9+\delta}$ [4,5] and $Tl_{0.8}Pb_{0.2}Bi_{0.2}Sr_{1.6}Ba_{0.4}Ca_2Cu_3O_{9+\delta}$ [14], have revealed ill-defined Tl-1223 grains [18] and little directional grain-alignment, but enhanced grain-connectivity. On the other hand, those with Sr:Ba = 1.8:0.2 have shown well-defined Tl-1223 platelets and a clear tendency of directional grain-alignment [7,17]. Thus a relatively high J_c of 2.5×10^4 A/cm^2 at 77 K and self-fields was obtained with excellent reproducibility in just-rolled tapes of $Tl_{0.8}Pb_{0.2}Bi_{0.2}Sr_{1.8}Ba_{0.2}Ca_{2.2}Cu_3O_{9+\delta}$ nominal composition [17]. The high J_c value was attributed to enhancement in grain-connectivity and degree of texture by using a newly proposed framework of grain-linking [19]. However, the strong field dependence of J_c in the tapes revealed the existence of significant weak-links [17]. Thus, for further enhancement of J_c, Tl-1223 grains need to be textured in the order of long range.

Recently, Hamdan et al. [20] reported that partial substitution of oxygen by fluorine in polycrystalline bulk of $Tl_{0.5}Pb_{0.5}Sr_{1.6}Ba_{0.4}Ca_2Cu_3O_{9+\delta}$ nominal composition resulted in an enhancement in superconducting properties such as T_c, intra-granular J_c and the reduc-tion of weak-links by partially replacing oxygen with fluorine.

The present study aims to fabricate the F-doped Ag/Tl-1223 tape that the enhance-ment of the superconducting properties is expected. Ag-sheathed tapes of $Tl_{0.8}Pb_{0.2}Bi_{0.2}Sr_{1.8}Ba_{0.2}Ca_{2.2}Cu_3O_yF_x$ $(0 \leq x \leq 1)$ nominal com-positions were prepared by using the PIT method. Then I_c, phases, morphology and the junction characteristic of inter-granular contacts in Tl-1223 tapes with different F content, which prepared using various thermo-mechanical treatments, were investigated and compared to those in a F-undoped tape.

Table 1. Variation of I_c with thermo-mechanical treatment in tapes of $x = 0.25$. The tapes were heat-treated at $800 \sim 820℃$ for 20 min, rolled and heat-treated again at $790 \sim 830℃$ for $4 \sim 7$ h.

1st heat-treatment temp./time	2nd heat-treatment (temp. & time)					
	790℃		800℃		820℃	830℃
	4 h	5 h	4 h	7 h	7 h	7 h
800℃/20 min	2.45 A	2.49 A	3.26 A	3.02 A	1.58 A	1.60 A
810℃/20 min	3.34 A	3.92 A	4.71 A	4.36 A	2.88 A	2.50 A
820℃/20 min	4.02 A	4.02 A	5.25 A	4.39 A	0.99 A	2.20 A

2. Experimental

F-doped Tl-1223 tapes of $Tl_{0.8}Pb_{0.2}Bi_{0.2}Sr_{1.8}$ $Ba_{0.2}Ca_{2.2}Cu_3O_yF_x$ $(0 \leq x \leq 1)$ nominal composi -tions were prepared using the PIT method incorporating an in-situ reaction method, as follows: In order to prepare prepowder $Sr_{1.8}$ $Ba_{0.2}Ca_{2.2}Cu_3O_yF_x$ $(x = 0.25,$ $0.5,$ 0.75 and $1.0)$, $SrCO_3$, $BaCO_3$, $CaCO_3$, CuO and CuF_2 powders were mixed in their stoichiometric ratio. The powder mixtures were heat-treated at $920℃$ for 48 h and pulverized with an intermediate grinding after 24 h heat-treat -ment. The powders were annealed at $700℃$ for 3 h in vacuum $(10^{-5}$ Torr), ground and sieved into particles less than 26 μm (500 mesh). Then Tl_2O_3, PbO and Bi_2O_3 powders were mixed with the prepowder The mixed precursors were filled into Ag tubes. The tubes were drawn and rolled to 0.5 mm thick. The rolled tape was cut to 1 m long and heat- treated in $800 \sim 840℃$ for 20 min. Then, the tape was rolled again to 0.095 ~ 0.115 mm thick and cut to pieces ~ 5 cm long. The tape pieces were heat-treated in $800 \sim 840℃$ up to 7 h. In some tapes, an intermediate rolling was incorporated during the final heat- treatment. The details on the tape prepara -tion were shown elsewhere [14,17].

I_c's of the tapes were evaluated using dc four-probe electrical measurement at 77 K. 1 V/cm was adapted to a criterion for I_c. Ac susceptibilities of the tapes were measured in a temperature range of 30-130 K using a Lake Shore 7000 series ac susceptometer. For the measurements, ac fields of $0.1 \sim 20$ Oe in intensity and 1,000 Hz in frequency were applied perpendicular to the tape surface. The phases in the tape cores were examined using a Rigaku X-ray diffractometer with $CuK\alpha$ radiation. The tape core morphology was investigated using a scanning electron micro- scope (Hitachi S-4200) with an accelerating voltage of 20 kV.

3. Results and discussion

Fig. 1 shows variation of XRD pattern with F content in prepowder of $Sr_{1.8}Ba_{0.2}Ca_{2.2}$ $Cu_3O_yF_x$ $(x = 0.25,$ $0.5,$ 0.75 and $1.0)$. The prepowder of $x = 0.25$ is consisted of $CuSrO_2$, Ba_2CuO_3, CaO_2 and minor phases of $Ca_{0.4}Cu$ $Sr_{0.4}O_2$, Ba_3CuO_4 and $Sr_{14}Cu_{24}O_{41}$, as similar with F-undoped prepowder [14]. In the prepowder of $x \geq 0.5$, however, $Ca_{0.4}CuSr_{0.4}O_2$ appears to be a major phase. The amounts of SrF_2, $Ba_6Cu_7F_{26}$ and $Sr_{14}Cu_{24}O_{41}$ phases increase with F content, while $CuSrO_2$ and CaO_2 decrease. The different phase contents depending on F content indicates that different chemical reaction occurred depending on F content.
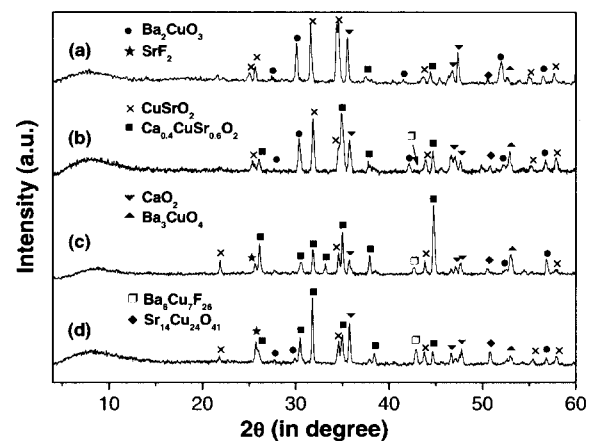

Fig. 1. Variation of XRD pattern with F content in prepowder $Sr_{1.8}Ba_{0.2}Ca_{2.2}Cu_3O_yF_x$ $(x = 0.25,$ $0.5,$ 0.75 and $1.0)$. (a) $x = 0.25$, (b) $x = 0.5$, (c) $x = 0.75$ and (d) $x = 1.0$.

When the tapes were heat-treated at $830 \sim$ $840℃$, which is an optimum heat-treatment temperature range in F-undoped tapes, low I_c's less than 2 A were obtained regardless of F content. Relatively high I_c's were obtained

in tapes heat-treated at 790~820℃. An example is shown in Table 1. In Table 1, a relatively high I_c of 5.25 A at 77 K and self field was obtained in the tape heat-treated at 820℃ for 20 min, rolled and heat-treated at 800℃ for 4 h. When the tape was rolled and heat-treated again, I_c decreased to less than 3 A. That means that intermediate rolling at the final heat-treatment procedure, which resulted in a significant increase of J_c in a F-undoped tape, is not beneficial in obtaining high J_c in the present F-doped composition. Furthermore, I_c significantly decreased with increasing F content beyond x=0.25.

Fig. 2 shows the change in XRD pattern with F content in tapes heat-treated at 810℃ for 20 min, rolled and heat-treated again at 820℃ for 7 h. In tape of x=0.25, main Tl-1223 phase was formed with minor Tl-1212 phase. As F content increased, however, the ratio of Tl-1212 to Tl-1223 and the amount of SrF_2 increased. This implies that F doping suppressed the formation of Tl-1223 phase in the tape specimen. The decrease of Tl-1223 content with increasing F content seems to related to the increase in impurity phases content such as SrF_2 with F content. It seems that SrF_2 formed at the initial stage of reaction, remained or even increased through the repeated rolling and annealing processes. Therefore, it is thought that the formation of SrF_2 at the early stage of powder preparation changes the stoichiometric ratio of constituent cations, and consequently limits the amount of Tl-1223 which can be formed and results in a significant decrease in J_c.
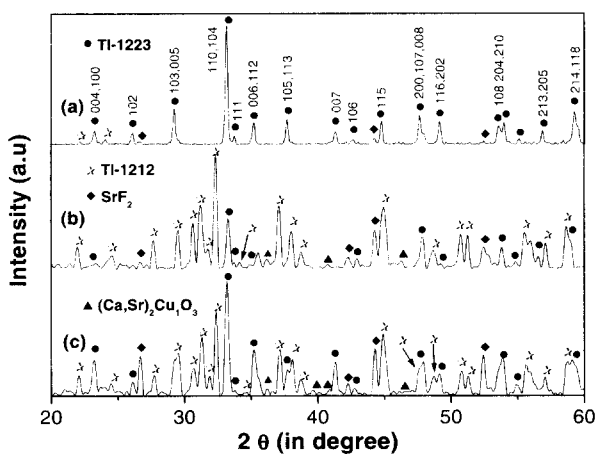
tape of x=0.25 with I_c of 4.71 A at 77 K and self field. The tape was heat-treated at 810℃ for 20 min, rolled and heat-treated again at 800℃ for 4 h. The figures show that Tl-1223 grains are platelets, indicating that the grain morphology was not significantly changed with F-doping, compared with the F-undoped tapes [17]. Actually the plate-like Tl-1223 grain shape was not changed even at F content up to x=1.0. It was found that, however, as the F content increased, the grains became thicker and impurities became abundant. In Fig. 3, the platelets seem to have a certain tendency of directional grain-alignment, but they are not strongly textured. Grain-linkage was not enhanced compared with in F-undoped tape [17]. There also exist many large pores and impurities, which are not beneficial to obtaining a high J_c.
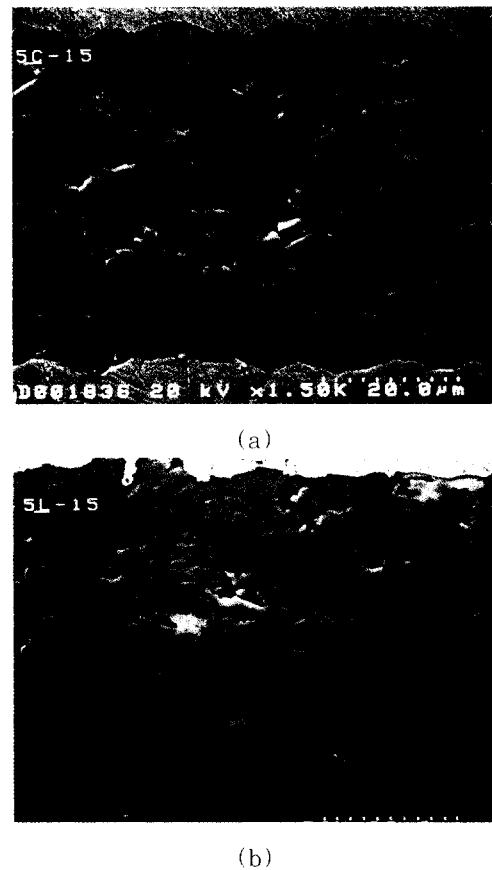

(a)

(b)

Fig. 3. SEM images taken in (a) transverse and (b) longitudinal cross-sections of tape of x=0.25 with I_c of 4.71 A at 77 K and self field. The tape was heat-treated at 810℃ for 20 min, rolled and heat-treated again at 800 ℃ for 4 h.

Fig. 4 shows variation of the temperature dependence of ac susceptibilities with the intensity of the applied ac field for the F-undoped (x=0) tape with a J_c of 25,200 A/cm^2 at 77 K and in a self field. The tape

Fig. 2. Variation of XRD pattern with F content in $Tl_{0.8}Pb_{0.2}Bi_{0.2}Sr_{1.8}Ba_{0.2}Ca_{2.2}Cu_3O_xF_x$ tapes. The tapes were heat-treated at 810℃ for 20 min, rolled and heat-treated again at 820℃ for 7h. (a) x=0.25, (b) x=0.5 and (c)x=0.75.

Fig. 3(a,b) shows SEM images taken in transverse and longitudinal cross-sections of

was heat-treated at 840℃ for 20 min, rolled, heat-treated at 840℃ for 4 h, rolled and heat-treated at 840℃ for 4 h again [17]. Fig. 5 shows variation of the temperature depen -dence of ac susceptibilities with ac field intensity taken in tape of x=0.25 heat -treated at 820℃ for 20 min, rolled, heat -treated at 800℃ for 4 h. Comparison of the real part of ac susceptibilities in Fig. 4 and 5 reveals that the volume percentage of super -conducting phases is much higher in the F-undoped tape (~83%) than in the F-doped tape of x=0.25 (~50%).
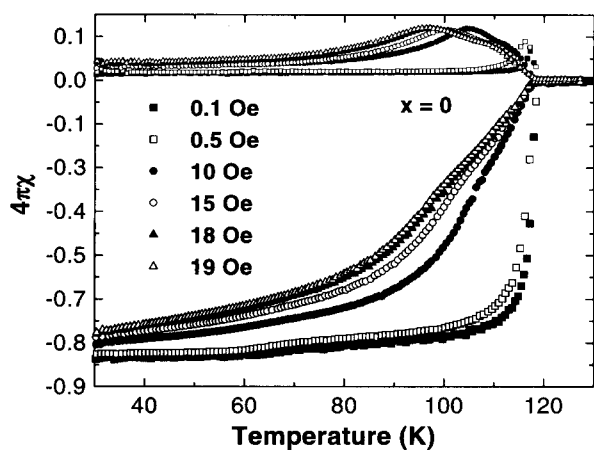

Fig. 4. Variation of the temperature depend- ence of ac susceptibilities with the intensity of the applied ac field for the F-undoped(x=0) tape.
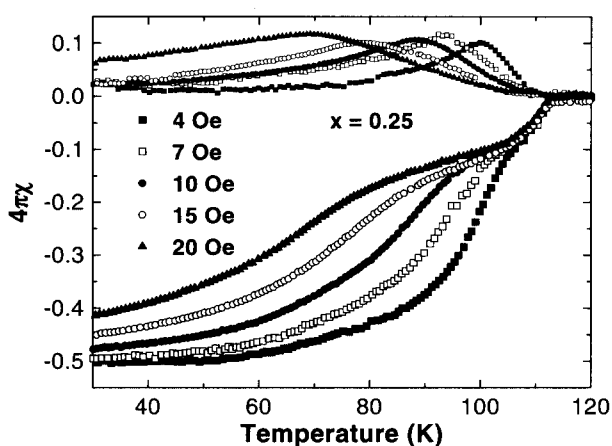

Fig. 5. Variation of the temperature depend- ence of ac susceptibilities with the intensity of the applied ac field for the tape of x=0.25. The tape was heat-treated at 820℃ for 20 min, rolled, heat-treated at 800℃ for 4 h.

Fig. 6 shows the dependence of T_c and peak temperature (T_p) of imaginary compo -nent of ac susceptibility on intensity of the ac field applied in tapes of x=0 and 0.25, which was obtained from Fig. 4 and 5. Fig. 6

shows that T_c in tape of x=0.25 is lower than that in F-undoped tape by 5.3 K, indicating that F-doping in the present composition decreases T_c. This result is not consistent in the result of Hamdan et al. [20].

It has been adopted that in a given ac field, a critical state is established at a temperature (T_p) where a peak in imaginary part of ac susceptibility appears. That means that the magnetic flux with a given field intensity penetrates into the center of inter-granular junction at T_p and thus a maximum ac loss generates. Therefore, T_p is a measure of inter-granular coupling strength. Comparison of the field dependence of T_p in both tapes in Fig. 6 indicates that the inter-granular coupling is stronger in tape of x=0 than in tape of x=0.25.
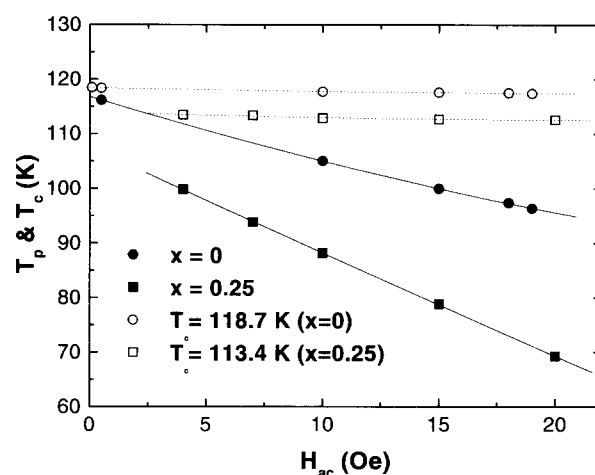

Fig. 6. The dependence of maximum ac loss temperature (T_p) and T_c on field in tapes of x=0 and 0.25. Circles represent for x=0 and squares for x=0.25. Closed ones represent for T_p and open for T_c.
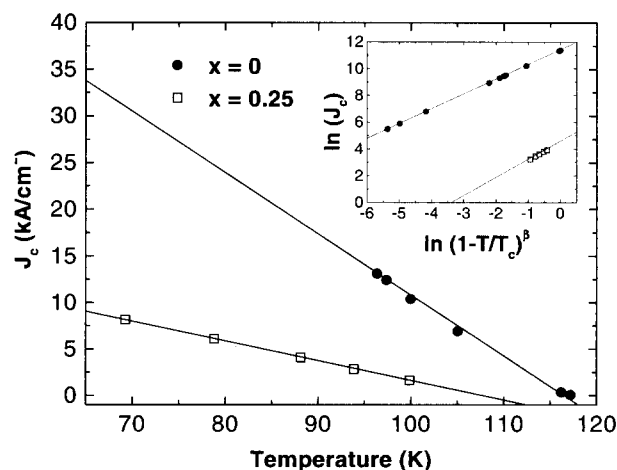

Fig. 7. The temperature dependence of the inter-granular $J_{c,J}$, which is calculated by applying Beans formula $J_c = H_p/a$ to the critical state. The inset shows a plot of the calculated $J_{c,J}$ versus $(1-T/T_c)^\beta$.

In the frame of the finite critical state model [21,22,23], the inter-granular critical current density ($J_{c,J}$) has been evaluated by applying Beans formula $J_c = H_p/a$ to the critical state. Here a is a sample dimension, and H_p is the critical field for which the flux just reaches the center of the sample and the intensity of the applied field at T_p. Fig. 7 shows the temperature dependence of $J_{c,J}$ values calculated using Beans formula. J_c's of 25,500 and 6,800 A/cm^2 at 77 K and 0 T were obtained for tapes of x = 0 and 0.25, respectively. These values are in an excellent agreement with the measured transport J_c. The inset in Fig. 7 shows a plot of the calculated $J_{c,J}$ versus $(1-T/T_c)^\beta$ [24,25]. ß was evaluated to be 1.1 and 1.05 for tapes of x = 0 and of x = 0.25, respectively, indicating that the inter-granular contacts in both tapes are basically a SIS Josephson junction type and SNS characteristic is a little stronger in the F-undoped tape.

4. Conclusion

F-doped Tl-1223 tapes of $Tl_{0.8}Pb_{0.2}Bi_{0.2}Sr_{1.8}Ba_{0.2}Ca_{2.2}Cu_3O_yF_x$ (x = 0.25, 0.5, 0.75 and 1.0) compositions were prepared using the PIT method and their characteristics were compared to those in a F-undoped tape. It was found that F-doping resulted in a decrease of the formation temperature of Tl-1223 phase, but accelerated the formation of the undesirable impurity phases. Also it resulted in the decrease in T_c, J_c and coupling strength in inter-granular junctions. The significant J_c decrease resulting from F-doping is attributed to much reduced Tl-1223 phase content caused by formation of undesirable impurity phases such as SrF_2. However, F-doping seems not to change the morphology of Tl-1223 grains and the junc -tional type of inter-granular contacts.

Acknowledgement

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